Bi surfactant control of ordering and surface structure in GaInP grown by organometallic vapor phase epitaxy

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The surfactant Bi has been added during organometallic vapor phase epitaxial growth (OMVPE) of GaInP using the precursor trimethylbismuth. The addition of a small amount of Bi during growth results in disordered material using conditions that would otherwise produce highly ordered GaInP. Significant changes in the surface structure are observed to accompany the disordering. Atomic force microscopy measurements show that Bi causes an order of magnitude increase in step velocity, leading to the complete elimination of three-dimensional islands for growth on singular (001) GaAs substrates, and a significant reduction in surface roughness. Surface photoabsorption measurements indicate that Bi reduces the number of $[\bar{1}10]$ P dimers on the surface. Secondary ion mass spectroscopy measurements reveal that the Bi is rejected from the bulk, even though it changes the surface reconstruction. Clearly, Bi acts as a surfactant during OMVPE growth of GaInP. The difference in band gap energy caused by the reduction in order parameter during growth is measured using photoluminescence to be about 110 meV for layers grown on singular substrates. Disorder/order/disorder heterostructures were successfully produced in GaInP with a constant solid composition by modulating the TMBi flow rate during growth. [S0021-8979(00)06119-3]

INTRODUCTION

CuPt ordering occurs in $Ga_{0.52}In_{0.48}P$ layers grown by organometallic vapor phase epitaxy (OMVPE) on (001)-oriented GaAs substrates.[1,2] The Ga and In atoms spontaneously segregate into alternating {111} monolayers. The ordering phenomenon has been studied by many researchers in the past decade because the properties of compound semiconductor alloys are determined by the atomic arrangement of the atoms in the solid. For example, the band gap energy of partially CuPt ordered GaInP grown by OMVPE has been shown to be as much as 160 meV lower than for disordered material of the same composition.[3,4] In addition, ordering can be used for the fabrication of heterostructures and quantum wells without changing the solid's composition. Thus control of ordering is important for solar cells,[5] visible light emitting diodes (LEDs),[6] and visible lasers.[7]

Ordering is of fundamental interest because it is closely connected with the surface structure during growth, and thus gives insight into surface processes. Although CuPt ordering is commonly observed in ternary and quaternary compound semiconductors, it is not a stable structure in the bulk.[8] Theoretically, the alternating surface stresses resulting from the formation of rows of $[\bar{1}10]$-oriented phosphorus dimers on the (2×4)-like reconstructed (001) surface thermodynamically stabilize the CuPt structure on the $(\bar{1}11)$ and $(1\bar{1}1)$ planes in the third layer below the surface.[6–8] This is verified by experiments showing a direct correlation between the concentration of $[\bar{1}10]$ P dimers and degree of order (S).[9]

Although the driving force for ordering is understood, the mechanism remains unclear, even though several speculative models have been proposed.[10] Besides the known role of surface reconstruction, surface steps may also play an important role in the ordering process. For example, [110] steps have been observed to assist the ordering process.[11] This is indicative of the importance of kinetic effects at the step edges on the ordering process under certain growth conditions.

Another factor having a strong effect on ordering is doping. The addition of the dopant Te was observed to increase the $[\bar{1}10]$ step velocity by a factor of 20. This was attributed to a marked change in group III adatom attachment kinetics at the step edge.[12–14] No change in surface photoabsorption (SPA) anisotropy at 400 nm was observed. Correlation between the CuPt order parameter and step velocity suggests that the kinetics at the step edge affect the change in ordering. This is one of the early examples of surfactant effects during OMVPE growth.

Surfactant effects related to the surface structure have been the object of study in both elemental[15,16] and III/V semiconductors.[17,18] Surfactants, surface-active substances, accumulate at the surface and alter the surface properties of many materials.[19] In general, elements with low solid solubilities and low vapor pressures are most likely to accumulate on the surface. Surfactants that float on the surface with high concentrations can alter the surface structure during epitaxial growth.

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The addition of dopants during molecular beam epitaxial (MBE) growth of group IV semiconductors has been shown to affect the both adatom attachment at step edges[20,21] and surface reconstruction.[22,23] The surfactant Bi, a donor in the elemental semiconductors, has been used to produce atomically abrupt Si/Ge/Si heterointerfaces.[24] In addition, Bi has been reported to alter the surface structure of Si resulting in a $(2\times n)$ Bi–Si (001) reconstruction with two layers of Bi terminated by dimers.[25] In III/V semiconductors, isoelectronic As, Sb, and Bi also act as surfactants. Arsenic has been shown to modify the surface reconstruction of cubic GaN.[26] The surfactant Sb was found to change the surface reconstruction and control the band gap energy of GaInP grown by OMVPE.[27] Bi has been shown to modify the surface morphology of wurtzite GaN films.[28]

The purpose of the work reported here was to study the effects of the isoelectronic surfactant Bi on ordering and on the surface structure of GaInP grown by OMVPE. Bismuth is expected to behave as a surfactant, since it is relatively involatile and has a much greater covalent radius than P and will likely be rejected from the solid.[29] A secondary purpose was to demonstrate that the surfactant Bi is effective in controlling the band gap energy so it can be used to make heterostructures by modulating the trimethylbismuth (TMBi) flow rate during growth.

EXPERIMENT

$Ga_{0.52}In_{0.48}P$ layers were grown in a horizontal, infrared-heated, atmospheric pressure OMVPE system on semi-insulating (001) singular GaAs substrates with GaAs buffer layers, as described previously.[30] The substrates were prepared by standard degreasing followed by a 1 min etch in a $12H_2O{:}2NH_4OH{:}1H_2O_2$ solution. They were then rinsed for 5 min in de-ionized water and blown dry with filtered N_2 gas before being loaded into the reactor. Two reactors were used for the growth runs. In one reactor, trimethylgallium (TMGa) at $-7.2\,^{\circ}C$ and trimethylindium (TMIn) at $25.4\,^{\circ}C$ were used as the group III precursors. Phosphine (PH_3) was used as the group V precursor. TMBi at $-7.2\,^{\circ}C$ was used as the Bi precursor. All of the layers were grown at $620\,^{\circ}C$ with a PH_3 partial pressure of 3 Torr, for a V/III ratio of 80, and a total flow rate of 4400 ml/min. The growth rate was constant at approximately 1.3 μm/h. An undoped, ordered GaInP layer approximately 0.22 μm thick was grown followed by a $\sim$0.43 μm GaInP layer grown with TMBi. In order to obtain sufficiently low Bi concentrations, a reduced duty cycle of TMBi flow was sometimes used (for example, 20 s of TMBi flow out of every 60 s of growth). The other reactor contains a built-in optical system for SPA measurements. For this system, the In precursor was solution TMIn, the growth rate was 1.32 μm/h, and the phosphorus precursor was tertiarybutylphosphine (TBP). The TBP partial pressure and V/III ratio were kept constant at 1.0 Torr and 40, respectively. The growth conditions for the two reactors were similar.

In the reactor with the SPA system, chopped, *p*-polarized light from a 150 W Xe lamp was used to irradiate the surface of the sample in the direction of the gas flow at the Brewster angle (approximately 70°).[31] The SPA measurements were performed at $620\,^{\circ}C$. The reflected light was dispersed by a compact monochromator and detected with a Si pnn^+ photodiode using standard lock-in amplifier techniques. SPA measurements were made on the layers with the light parallel to the $[\bar{1}10]$ and $[110]$ directions. The solid compositions of the GaInP layers were determined by x-ray diffraction data using Vegard's law. All samples were confirmed to have a mismatch of $<0.1\%$.

Photoluminescence (PL) measurements were performed at 20 K. The 488 nm line of an Ar^+ laser with a power of 10 mW focused to a 0.5 mm^2 spot was used to excite the samples. The PL signal was dispersed with a SPEX monochromator and detected with a photomultiplier tube using standard lock-in amplifier techniques. The low temperature PL peak energy was used to determine the degree of order, *S*, using the following equation:[32]

$$\text{degree of order}\,(S) = \sqrt{\frac{2005 - \text{PL peak energy at 20 K (in meV)}}{471}}, \qquad (1)$$

where 2005 meV is the band gap of completely disordered GaInP and 471 meV is the maximum change in the band gap energy for perfectly ordered GaInP.

The surface morphology, including the step structure, was characterized using a Nanoscope III atomic force microscope (AFM) in tapping mode. Etched single-crystalline Si tips were used that had an end radius of about 5 nm and a sidewall angle of about 35°. Scan rates of 1–2 lines per second were used and data were taken at 512 points/line and 512 lines/scan areas. The samples were measured in air, so were covered by a thin, conformal oxide layer. [110] cross-section transmission electron microscope (TEM) samples were prepared using standard Ar^+-ion milling at 77 K. The transmission electron diffraction (TED) patterns and TEM images were obtained using a JEM 2010 scanning TEM operated at 200 kV. The secondary ion mass spectroscopy (SIMS) depth profiles of GaInP layers grown with the addition of TMBi were performed by Applied Microanalysis Labs.

RESULTS

A 1.3 μm thick disorder/order/disorder (D/O/D) GaInP heterostructure was grown on a singular GaAs substrate with and without the addition of Bi during growth. A Bi/III ratio of 1.65×10^{-2} in the vapor was used to produce the disordered layers. The first disordered GaInP layer was grown with TMBi for 10 min. The TMBi flow was then turned off for 35 min to grow the undoped GaInP layer. The second disordered layer was then grown with the addition of TMBi for another 10 min. It is important to note that no change in the GaInP solid composition was observed due to Bi, hence no adjustment of the Ga/In ratio in the vapor was required to obtain samples with lattice-matched heterostructures. Figure 1 shows a cross-sectional, [110] dark field (DF) TEM image of the D/O/D heterostructure. In this image, the ordered layer appears brighter than the disordered layer. Within the ordered region, there are inclined dark lines corresponding to antiphase boundaries (APBs). The TEM DF image clearly

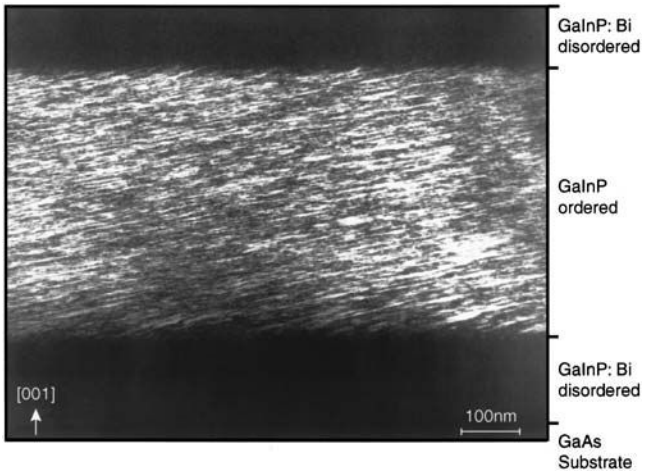

FIG. 1. Dark-field TEM [110] cross-sectional image of a disorder/order/disorder GaInP heterostructure grown on a singular (001) GaAs substrate. The middle layer was grown without TMBi and the other two layers were grown with $(Bi/III)_v = 1.65\times10^{-2}$. The addition of a small amount of Bi suppresses the ordering.

shows that ordering was suppressed by the addition of a small amount of Bi during growth: D/O/D heterostructures can be successfully produced by simply modulating the TMBi flow.

SIMS depth profiles of D/O/D and O/D/O structures demonstrated that the concentration of Bi incorporated into the layer is below the detection limits of $\sim 10^{16}$ cm^{-3}. However, the Bi concentration on the surface was large. It is obvious that Bi is a highly effective surfactant for the OMVPE growth of GaInP layers.

The 20 K PL peak energy was used to estimate the band gap energy for the GaInP layers, all lattice matched to the GaAs substrates. Figure 2 shows the degree of order versus the Bi/III ratio in the vapor. It is seen that an increase in the Bi/III ratio results in a decease in the degree of order. Note

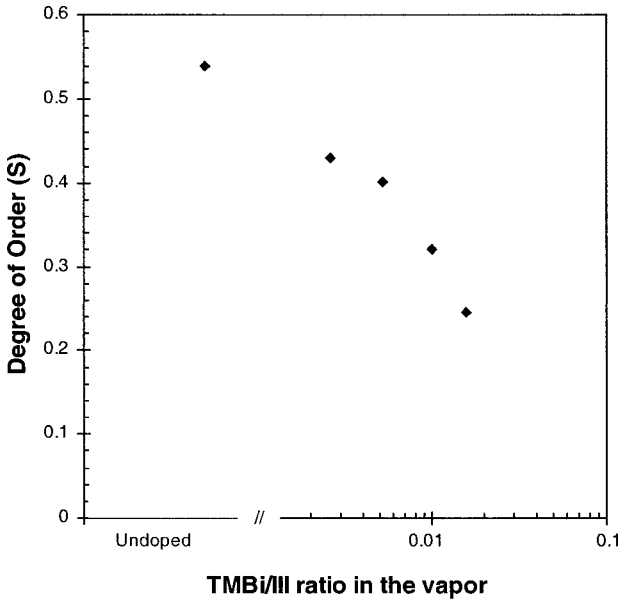

FIG. 2. Degree of order (S) vs the ratio of Bi to [Ga+In] in the vapor $(Bi/III)_v$.

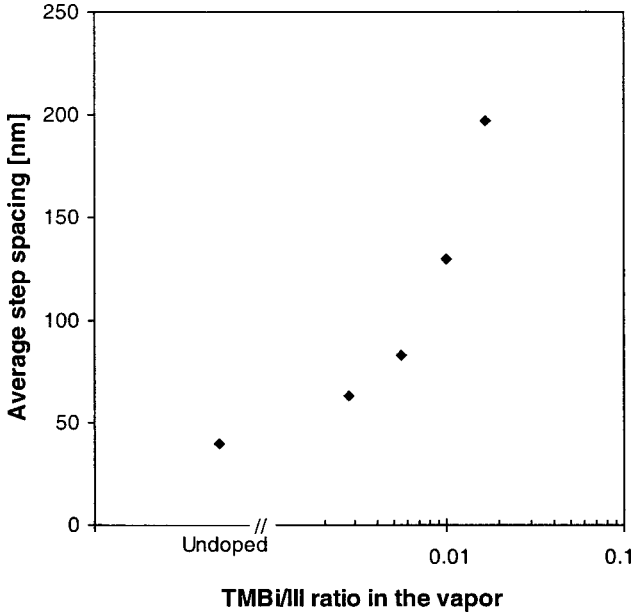

FIG. 3. Step spacing vs $(Bi/III)_v$ showing that the step spacing increases with increasing TMBi in the vapor.

that only a small amount of Bi $[(Bi/III)_v = 1.65\times10^{-2}]$ is required to reduce the degree of order (S) to approximately 0.2. This result clearly demonstrates that Bi effectively destroys ordering in GaInP, in agreement with the TEM results presented in Fig. 1.

Figure 3 shows a plot of the average step spacing of GaInP grown on singular substrates versus the Bi/III ratio in the vapor. The average step spacing was obtained by carefully counting the average step spacing along ten 1 μm AFM profiles. Increasing the Bi/III ratio from 0 to 1.65×10^{-2} causes the average step spacing to increase by about an order of magnitude. Elongation of islands in the $[\bar{1}10]$ direction due to an increase in the [110] step velocity was clearly observed in the AFM images.[33] The addition of Bi produces much smoother surfaces. The data were similar for the two reactors. By comparing the data in Figs. 2 and 3, it is seen that the increase in the step spacing coincides with the decrease in the degree of order. It is important to note that the effect of Bi on step structure is comparable to the results for Te concentrations exceeding 10^{18} cm^{-3} in GaInP.[14] For Te, the step spacing between [110] steps increased by approximately a factor of 20.

The SPA anisotropy spectra for GaInP with and without Bi on singular GaAs substrates are shown in Fig. 4. The positive peak at about 400 nm is attributed to P dimers aligned along the $[\bar{1}10]$ direction.[9] This surface is referred to as ''(2×4) like,'' since long range periodicity cannot be determined from optical measurements. After Bi was added for 15 min with $(Bi/III)_v = 1.0\times10^{-2}$, the intensity of the SPA anisotropy signal at 400 nm dropped to nearly zero. This apparently indicates that Bi on the surface reduces the $[\bar{1}10]$ P dimer concentration.

DISCUSSION

The effects of adding Bi during the OMVPE growth of GaInP on (001) singular GaAs are significant. The degree of

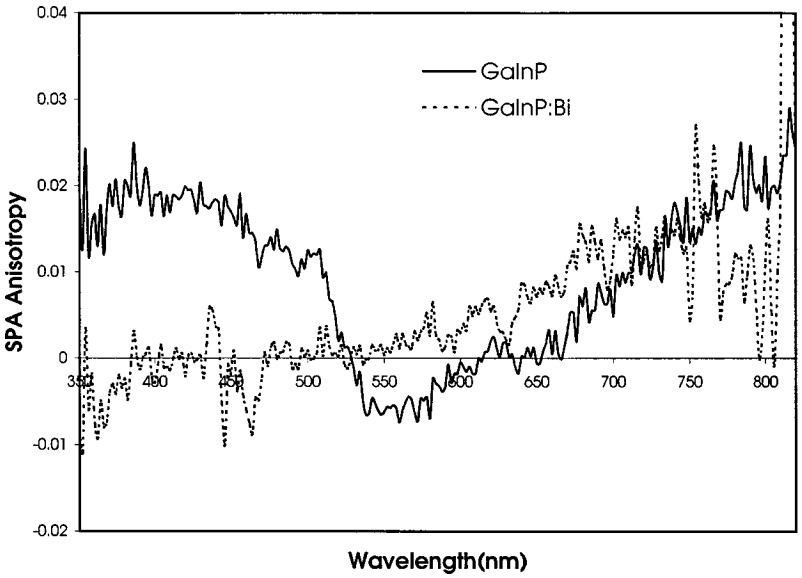

FIG. 4. SPA anisotropy spectra for GaInP layers grown with (dashed line) and without (solid line) Bi.

order of GaInP is changed from 0.53 to 0.2 by increasing the TMBi flow rate [from $(\mathrm{Bi/III})_v = 0$ to 1.65×10^{-2}]. This degree of order change corresponds to a difference in band gap of approximately 110 meV between GaInP layers grown with and without Bi. Room temperature Hall effect measurements were performed on undoped GaInP layers and disordered layers produced by the addition of TMBi during growth. Undoped GaInP layers were *n* type. Layers grown with Bi were *n* type with a slightly lower carrier concentration. The addition of Bi during growth does not result in a significant change in the Fermi level of GaInP. These results demonstrate the potential of Bi for the production of atomically engineered structures for advanced electronic and photonic devices. The ability to independently modulate the band gap and the Fermi-level position, since Bi is isoelectronic with P, is key to the potential usefulness of this technique.

In addition to the 110 meV band gap energy difference, dramatic changes in surface structure, i.e., step structure and surface reconstruction, are produced by the addition of Bi during growth. The average step spacing increases by an order of magnitude as the surfactant Bi is introduced into the growth system, resulting in the complete elimination of the island structure on the surface and a much smoother surface.[33] There is a significant step structure difference between the effects of isoelectronic surfactants Bi and Sb. The surfactant Sb increases step spacing only slightly but, as shown in Fig. 3, Bi increases the step spacing tenfold.[34]

The SPA anisotropy at 400 nm for $(\mathrm{Bi/III})_v = 1.0 \times 10^{-2}$ reveals that the concentration of $[\bar{1}10]$ P dimers has been reduced significantly when a small amount of Bi is added. Since the $[\bar{1}10]$ P dimers produce the surface driving force for CuPt ordering during growth, the reduction of the P dimer concentration by adding Bi during growth apparently eliminates ordering. This confirms previous results where the degree of order in GaInP was observed to be directly related to the P dimer concentration on the surface.[9] The low volatility of Bi and the rejection of Bi from the solid lead to the accumulation of Bi on the surface, as confirmed by the SIMS measurements.

As discussed above, a second factor known to suppress CuPt ordering is an increase in step velocity during growth. Ordering requires the ability of Ga and In atoms to exchange positions repeatedly at step edges. This is favored by small sticking coefficients.[21] In the extreme case, group III adatom sticking coefficients of unity would result in a completely random alloy.[12,14] Thus, the observed increase in step velocity is a second possible reason for the reduction in *S*. A comparison of Figs. 2 and 3 indicates an apparent correlation between the step spacing and the degree of order. The concentration of Bi where the step spacing begins to increase coincides with that at which the order parameter begins to decrease. This indicates that the suppression of ordering induced by Bi coincides with the increased sticking coefficients of Ga and In at the step edges, similar to the effect of Te described above. However, a significant difference is that Bi affects mainly the [110] step spacing while Te affects mainly the $[\bar{1}10]$ steps; Sb does not affect the step spacing significantly.[34]

CONCLUSIONS

The surfactant Bi has been used to control both the surface structure and ordering during OMVPE GaInP growth. The 20 K PL peak energy increased approximately 110 meV with the addition of Bi to the system. AFM measurements showed that the step spacing increased by a factor of 10 when Bi was added to the system, leading to the complete elimination of three-dimensional islands for the layers grown on singular (001) GaAs substrates. It has been shown that the surface reconstruction changes, reducing the driving force for formation of CuPt ordering. However, since the [110] step velocity increases by an order of magnitude with the addition of Bi, it is not possible to make a determination as to which mechanism is responsible for the disordering of GaInP.

Modulating the TMBi flow rate was successfully used to produce a disorder/order/disorder heterostructure with no change in the solid composition. SIMS measurements revealed that very little Bi was incorporated into the solid, i.e., it is an effective surfactant during OMVPE growth. The surfactant Bi might be an attractive choice to produce complex two-dimensional structures, such as heterostructures and quantum wells.

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